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Direct Preparation of Phosphoric Acid From Intermediate-Grade Western Phosphatic Shale

By Philip C. Good, T. N. Goff, and C. B. Daellenbach

UNITED STATES DEPARTMENT OF THE INTERIOR

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DIRECT PREPARATION OF PHOSPHORIC ACID FROM INTERMEDIATE-GRADE WESTERN PHOSPHATIC SHALE

by

Philip C. Good,[1] T. N. Goff,[1] and C. B. Daellenbach[2]

ABSTRACT

The Bureau of Mines investigated the feasibility of utilizing low-grade phosphatic shale as a feed for phosphoric acid production. Present practice in the phosphate mining operations of southeastern Idaho is to remove and either stockpile or waste low-grade phosphatic shales as the high-grade phosphate beds are selectively mined.

Acid digestion studies were performed on uncalcined shale and on shale calcined to remove free carbon to determine phosphoric acid quality, yield, and amenability to filtration. The untreated shale, containing 21.4 pct P_2O_5, was digested with sulfuric acid in a single-tank reactor to yield phosporic acid and gypsum residue. Although 96 pct P_2O_5 recovery was attained in digesting uncalcined shale, only the calcined product gave satisfactory filtration rates.

Calcined shale yielded phosphoric acid recovery of about 93 pct of the contained P_2O_5. It was higher in impurities than commercially prepared acid derived from high-grade western phosphate rock. An acid filtration rate of 745 lb $P_2O_5/ft^2/day$ was attained. This value is lower than the rate of 900 lb P_2O_5/ft^2 that is generally considered to be acceptable in industrial production of phosphoric acid from high-grade phosphate rock.

INTRODUCTION

This research work was carried out in accordance with Mines goals oriented toward utilizing low-grade mineral sources to extend domestic reserves. The bench-scale, continuous-circuit studies reported here are an extension of those carried out earlier on direct digestion of Florida phosphate matrix (1, 4-5).[3] These earlier studies involved the laboratory development of a digestion technique that would potentially permit direct

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[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

utilization of Florida phosphate matrix as a feed for phosphoric acid production. Direct use of matrix as a feed would eliminate the beneficiation steps that are normally necessary in preparing phosphate rock concentrates. If this processing method can be perfected further and scaled up to a commercial size, the production and disposal problems associated with the voluminous clay slimes (3) generated in conventional beneficiation can be avoided. Both the present study and earlier studies focused on perfecting the digestion operation. However, phosphoric acid produced in these studies has been generally higher in impurities than normally acceptable for commercial operations, and acid purification studies are currently in progress.

The purpose of the present investigation was to determine whether the bench-scale techniques found to be successful in digesting low-grade Florida matrices could be extended to other off-grade phosphatic materials. The material selected for this investigation is representative of an intermediate-grade (18 to 24 pct P_2O_5) shale which is separated during selective mining of high-grade, direct-use phosphate rock in Idaho. Although not currently processed, this product has in some cases been stockpiled for many years; current stockpiles are estimated to exceed 30 million tons. Studies (2) have been made to establish beneficiation requirements for upgrading shale to current direct-use specifications. The work described here, however, bypasses the beneficiation steps and treats the shale directly as a source of phosphoric acid.

The chemistry of sulfuric acid digestion of phosphate rock involves dissolution of the contained phosphatic mineral, which is generally collophane, a hydrated cryptocrystalline form of fluorapatite ($Ca_{10}[PO_4]_6F_2$). In the course of digestion with sulfuric acid (H_2SO_4), the phosphate values go into solution as phosphoric acid (H_3PO_4), and the contained calcium is precipitated as calcium sulfate dihydrate (gypsum, $CaSO_4 \cdot 2H_2O$).

The principal difficulty associated with any sulfuric acid digestion of phosphate rock lies in establishing those digestion conditions that lead to crystallization of the gypsum in a coarse, readily filterable form. If this is not done, it forms a fine, slimy mush which is slow to filter and difficult to wash.

The digestion studies on phosphatic shale were carried out in a single-tank, continuous-circuit reactor of about 1.8-kg/hr feed capacity. The unit had proved to be the most efficient reactor tested on Florida matrices because it permitted growth of large, rapid-filtering gypsum crystals (1).

EXPERIMENTAL PROCEDURES

Material and Preparation

An intermediate-grade phosphatic shale, supplied from a stockpile located in southeastern Idaho, was the raw material for this study. It consisted of dry, rather soft rock crushed to approximately minus 13 mm. Chemical analysis of the material is shown in table 1.

TABLE 1. - Analysis of phosphatic shale

P_2O_5.....pct..	21.4	SiO_2.....pct..	28.3
CaO.....pct..	32.1	MgO.....pct..	1.5
Fluorine.....pct..	2.5	Vanadium.....pct..	.09
Al_2O_3.....pct..	3.6	Free carbon..pct..	3.2
Fe_2O_3.....pct..	1.2	Uranium.....ppm..	27

In preparation for digestion, 15-kg batches of both uncalcined and calcined shale were dry-ground in a 32-cm-diameter rodmill. Grinding time was adjusted so that approximately 50 pct of the ore passed a 0.074-mm (200-mesh) sieve.

Equipment and Procedures

Two series of tests were conducted on this material. In the first, the as-received, dry-ground phosphatic shale was digested without further treatment. The second test series was performed using phosphatic shale that had been dry-ground and calcined at about 700° C to remove free carbon.

Continuous-circuit digestion studies were carried out in the same 12-liter single-tank reactor used for Florida matrix digestion (1). A diagrammatic flowsheet of the procedure is shown in figure 1. This reactor, constructed of type 316L stainless steel, utilized a central draft tube with a down-thrusting propeller to achieve thorough circulation of the digestion slurry. A water jacket surrounded the reactor, through which thermostatically controlled hot water was circulated to maintain the desired operating temperature. Dry feed entered the reactor from a belt feeder by falling directly on the top of the circulating slurry, whence it was drawn into a central vortex and rapidly distributed throughout the slurry. Sulfuric acid metered to the reaction was first mixed with weak "recycle" phosphoric acid (No. 2 filtrate) derived from countercurrent washing of the filter cake. The acid mixture passed through a tube into a zone of maximum turbulence near the bottom of the reactor. By introducing the dry feed and the acid at different locations in the reactor, they were separated until each had been thoroughly dispersed in the slurry.

During operation, digested slurry flowed continuously into a holding tank maintained at about 75° C, the purpose of which was to accumulate slurry for batch filtration. A filtration batch consisted of about 8 kg of slurry and formed, on a 34-cm-diameter filterpan, a cake about 3.5 cm thick. This was displacement-washed in three stages countercurrently with two weak acid solutions from the previous batch and with 2,750 ml of water as a finishing wash. This filtration system simulated that used on the industrial scale on rotating Prayon[4] pan filters. The filter medium used was a twill-weave polypropylene fabric, 59 by 28 count, weighing 9 oz/yd^2. Vacuum was maintained at 440 to 490 mm of mercury in accordance with industrial practice.

[4]Reference to specific equipment does not imply endorsement by the Bureau of Mines.

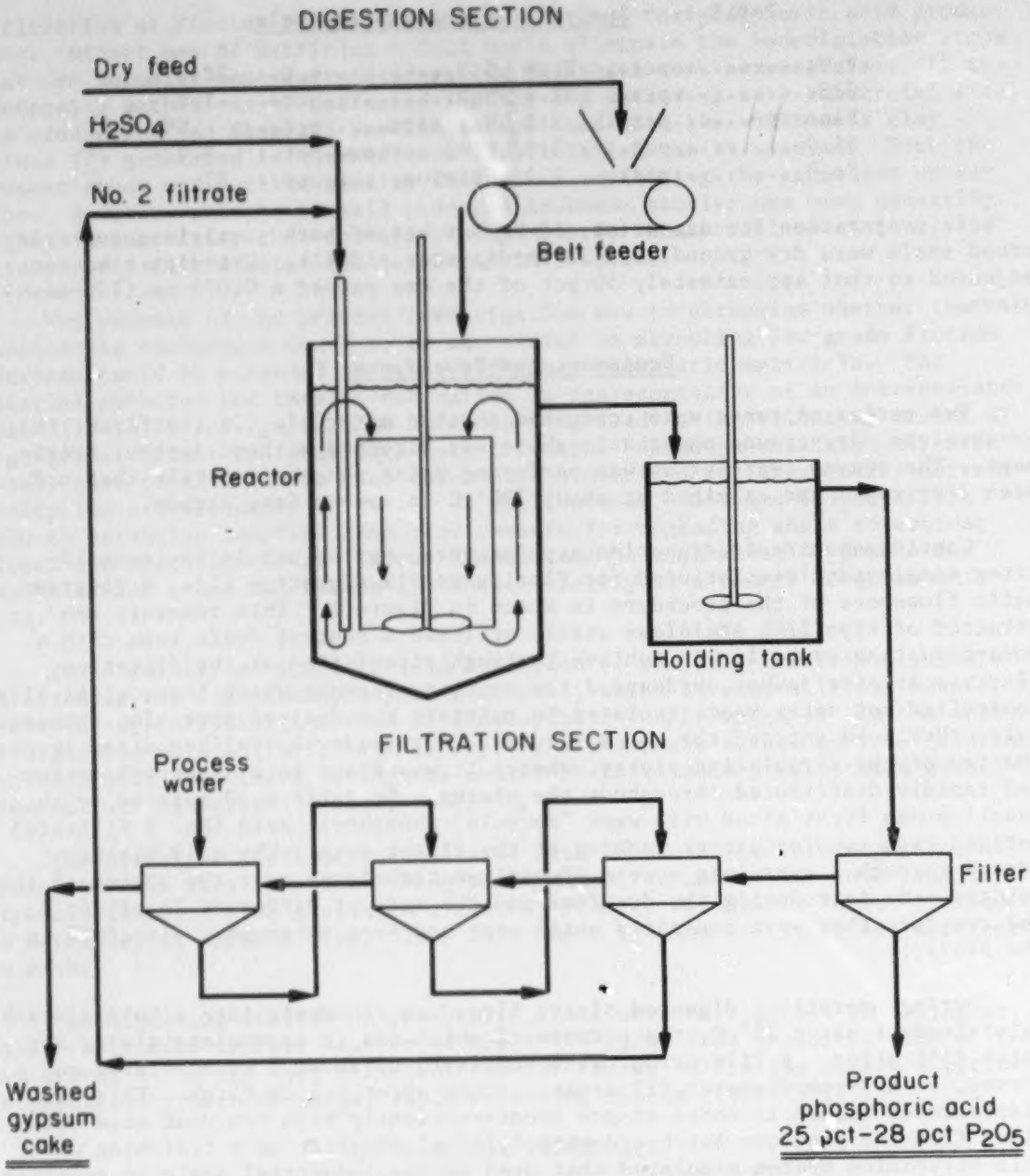

FIGURE 1. - Flow diagram, direct digestion of phosphatic shale.

The countercurrent filter-cake-washing system yielded three fractions. The first filtrate was the product acid. The No. 2 filtrate, designated "recycle acid," was a weak solution of phosphoric acid having a specific gravity of about 1.2. It was returned to the digestion step where it was metered,

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together with concentrated sulfuric acid, to the digestion reactor. Solutions 3 and 4 were reserved for washing the next filtration batch, and the final fraction was the washed filter cake, which was weighed, dried, and sampled for analysis.

Standardized filtration rate tests (1) were carried out in a filter funnel of 86-mm diameter, using a 2 by 2 twill-weave multifilament polypropylene cloth, 59 by 28 count, weighing 9 oz/yd^2. Vacuum was maintained at 440 mm of mercury in accordance with large-scale industrial practice. The slurry and all wash solutions were maintained at approximately 75° C.

In this equipment a 350-ml sample of slurry yielded a 3.6-cm-thick cake. This cake thickness was selected as a standard after communication with a large industrial firm producing phosphoric acid. They reported that a 3.6-cm cake thickness was used in their own laboratory filtration rate tests. The cake was filtered and was displacement-washed countercurrently in three stages, with a final wash of water. Time required for each step was recorded, and filtration rates were calculated by determining the weight, volume, and P_2O_5 content of the filter acid, the dry weight of the washed cake, and the sum of the filtration time, the three-stage wash times, ahd the cake dewatering time.

Earlier work (1, 5) had established that the use of a flocculant in slurry filtration of matrix yielded improved filtration rates. Very few flocculants were found to be effective. The best was a nonionic flocculant designated Nalco 8861. This flocculant was also effective in improving the filtration rate of slurry prepared from phosphatic shales. Dilute solutions of the flocculant were rapidly stirred into the slurry immediatedly prior to filtration at a dosage of 0.04 lb flocculant per ton of slurry (0.44 lb flocculant per ton of P_2O_5 in acid).

Reactor Operating Conditions

Previous studies had established the following conditions as yielding optimum results in digesting Florida matrix:

Matrix feed rate.....g/hr..	1,800
Free sulfate..... g/l..	30-40
Slurry density.....g/cm^3..	1.7-1.9
P_2O_5 in acid.....pct..	28-30
Temperature.....°C..	85

Initially, the same conditions were used in digesting the phosphatic shales. It was found that a small proportion of the gypsum crystallized as the undesirable fine-grained hemihydrate under these conditions. The digestion temperature was lowered to 75° C, and no further hemihydrate formation took place.

Free sulfate level, controlled by the rate of sulfuric acid addition, was monitored at intervals of 15 to 30 min. For sulfate determinations (5), barium chloride ($BaCl_2$) was added to a filtered sample of acid from the reactor,

and the volume of barium sulfate ($BaSO_4$) precipitate was measured after centrifuging; this is a widely used empirical method. As in all wet phosphoric acid processes, free sulfate level was especially critical to gypsum crystal growth. If the level fell below about 25 g/l, rapid nucleation of gypsum crystals occurred, resulting in slow filtration. Above about 50 g/l, gypsum coating formed on collophane particles, interfering with dissolution of the mineral and leading to unstable operation. In a small system such as the one described here, considerable vigilance was necessary to keep fluctuation of digestion conditions to a minimum, and operator skill and experience were important factors in successful operation.

Slurry density was monitored at intervals of 3 to 4 hours. If slurry density, resulting principally from too high content of solids, exceeds about 1.9 g/cm^3, it causes interference with gypsum crystallization with an attendant drop in filtration rate. The slurry density of the reactor system was regulated by varying the rate of addition of recycle acid.

Gypsum crystal growth was monitored by periodically taking photomicrographs of the slurry. The effect of process variables on crystal growth and crystal habit could be quickly determined in this manner.

DIGESTION STUDIES

Studies were conducted on both uncalcined and calcined shale. Operating and chemical analysis data recorded at selected times during the continuous-circuit digestion operations are presented in tables 2 and 3. Each table includes two sets of data. The columns labeled "Date and time" consist of analytical and recovery information derived from phosphoric acid and residue prepared during the routine processing of reactor product slurries. For these, the residue was filtered and washed on the 34-cm-diameter filter. The columns headed "Pan" contain data derived from the standardized filtration rate procedures that were developed during Florida matrix studies (1).

TABLE 2. - Digestion of uncalcined phosphatic shale

	Date and Time		Pan 1
	6/17 8:30 a.m.	6/17 2:00 p.m.	
Extraction, pct:			
P_2O_5	96.0	96.5	97.3
F	41.7	41.8	68.1
Rejection, pct:			
Al_2O_3	33.6	45.0	32.0
Fe_2O_3	22.2	32.1	20.4
Filtration rate tests:			
Time, min	NAp	NAp	37.4
Filter acid, lb $P_2O_5/ft^2/day$	NAp	NAp	71
Solids, lb solids/ft^2/day	NAp	NAp	377
Filter acid:			
Weight, g	1,603	1,428	256.8
Volume, ml	1,170	1,040	204
Specific gravity	1.37	1.37	1.26
Analyses, g/l:			
P_2O_5	376.0	405.2	276.8
SO_4	32.0	40.4	35.8
F	17.6	19.3	16.5
MgO	14.8	15.9	10.9
CaO	1.8	1.4	1.7
Al_2O_3	23.0	25.3	16.5
Fe_2O_3	13.2	14.6	9.2
SiO_2	98.4	115.6	115.6
Filter cake:			
Dry weight, g	3,991	3,774	298.5
Moisture, pct	29.5	25.8	34.8
Thickness, cm	3.8	3.6	3.9
Analyses, pct:			
P_2O_5	0.5	0.4	0.5
F	0.7	0.7	0.5
Al_2O_3	0.3	0.6	0.5
Fe_2O_3	0.1	0.2	0.2
SiO_2	15.0	14.8	12.9

NAp Not applicable.

TABLE 3. - Digestion of calcined phosphatic shale

	Date and time								Pan	
	7/7 1:00 p.m.	7/8 10:00 a.m.	7/8 1:30 p.m.	7/11 10:30 a.m.	7/11 2:45 p.m.	7/12 3:25 p.m.	7/13 9:45 a.m.	7/13 11:00 a.m.	1	2
Extraction, pct:										
P_2O_5	91.5	93.0	93.2	93.6	92.8	92.3	91.9	93.5	94.7	93.8
F	59.6	59.4	68.0	68.4	57.2	51.0	51.4	58.7	51.9	68.3
Rejection, pct:										
Al_2O_3	39.6	37.6	36.7	34.3	39.6	44.7	42.2	40.4	33.6	36.5
Fe_2O_3	29.8	25.4	26.4	24.0	30.3	32.2	31.2	30.0	24.7	26.3
Filtration rate tests:										
Time, min	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	3.28	4.15
Filter acid lb $P_2O_5/ft^2/day$	NAp	NAp	NAp	NAp	NAp	NAp	NAP	NAp	784	706
Solids lb solids/ft^2/day	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp	3,250	2,540
Filter acid:										
Weight, g	1,665	1,963	1,740	1,928	1,840	1,680	1,938	2,150	200.3	275.6
Volume, ml	1,220	1,450	1,270	1,480	1,380	1,250	1,420	1,550	150	216
Specific gravity	1.37	1.35	1.37	1.30	1.33	1.34	1.37	1.39	1.34	1.28
Analyses, g/l:										
P_2O_5	368.6	355.2	366.2	343.5	359.2	339.0	355.3	355.3	363.3	287.6
SO_4	44.4	40.4	41.6	46.8	42.8	42.8	42.0	40.4	41.2	33.6
F	20.2	19.1	20.3	18.6	18.0	18.4	20.0	18.1	18.8	16.1
MgO	15.2	15.2	16.0	15.0	15.1	16.0	15.9	15.9	17.1	16.5
CaO	2.0	2.5	2.5	1.9	1.4	2.6	2.4	3.0	1.6	1.6
Al_2O_3	25.6	24.1	24.6	24.1	24.1	22.9	24.4	23.3	23.8	19.2
Fe_2O_3	13.2	13.2	13.6	13.0	13.2	11.7	12.4	12.2	11.9	9.5
SiO_2	18.4	19.1	19.2	19.1	17.8	10.4	11.3	11.1	10.1	10.1
Filter cake:										
Dry weight, g	3,250	3,101	2,692	2,777	3,162	2,788	3,275	3,125	225.8	223.4
Moisture, pct	35.2	32.9	38.5	33.4	27.3	34.2	32.3	32.9	30.7	29.0
Thickness, cm	3.7	3.6	3.4	3.5	3.6	3.2	3.7	3.4	3.5	3.5
Analyses, pct:										
P_2O_5	1.3	1.3	1.3	1.3	1.2	1.3	1.4	1.3	1.3	1.4
F	0.7	0.6	0.5	0.5	0.6	0.8	0.8	0.7	0.7	0.5
Al_2O_3	0.6	0.7	0.7	0.7	0.7	0.8	0.7	0.9	0.8	0.8
Fe_2O_3	0.2	0.2	0.2	0.2	0.3	0.3	0.2	0.3	0.3	0.2
SiO_2	39.0	40.1	39.3	39.6	38.8	40.3	40.6	40.3	41.3	40.3

NAp Not applicable.

Digestion of Uncalcined Phosphatic Shale

Digestion studies were initiated on untreated ground shale having a free carbon content of 3.2 pct. Although it was anticipated that frothing in the reactor might be a problem because of the high carbon content, no such difficulty was encountered.

After stable operating conditions were established in the reactor, large gypsum crystals formed in the slurry (fig. 2A). The formation of these large crystals did not, however, result in an easily filterable slurry. Results of this series of digestion tests are shown in table 2. During these tests, H_2SO_4 consumption was about 3.6 lb H_2SO_4/lb P_2O_5 in uncalcined feed. Phosphoric acid filtered from the reactor residue contained about 96 pct of the P_2O_5 in the feed. Although P_2O_5 extraction was very high, the filtration rate of the slurry was not only erratic, but was too low for practical application of the system. A filtration rate of about 70 lb P_2O_5/ft^2/day was obtained. The slow filtration was attributed to the comparatively large quantity of fine carbon in the slurry, which may have caused blinding of the filter cloth and limited drainage of the cake.

FIGURE 2. - Photomicrographs of gypsum residue. *A*, Uncalcined shale; *B*, calcined shale.

To test this hypothesis, for the next test series, a quantity of shale was calcined. Calcination conditions were designed to remove as much carbon as possible from the ore without reaching temperatures (900° to 950° C) that are known to seriously inactivate phosphate rock to dissolution by H_2SO_4.

Calcination of Phosphatic Shale

Phosphatic shale was crushed to a nominal minus 5-mm size and passed through a small, externally heated rotary kiln. Residence time was about 15 min at 700° C. Examination of the calcined material showed that larger particles, which had turned from black to pale gray, remained black in the interior, showing that oxidation had only taken place in a surface layer. The calcined product was then screened, and the minus-1.7-mm (10-mesh) fraction, which was the approximate maximum size of fully calcined material, was set aside. The oversize fraction was crushed to minus 1.7 mm and again passed through the kiln at about 700° C. The product of this second calcination was blended with undersize of the first calcination to yield a master feed product. This calcined product contained 0.57 pct free carbon. In preparation for digestion it was further dry-ground in the same manner as the uncalcined material so that 50 pct of the material passed a 0.074-mm sieve.

Digestion of Calcined Phosphatic Shale

Digestion of the calcined shale was carried out according to the same procedure utilized in digesting the uncalcined material. No significant operating differences were noted. Results of digesting the calcined product are shown in table 3, and crystal form and size are shown in figure 2B. Sulfuric acid consumption was about 3.0 lb H_2SO_4/lb P_2O_5 in the calcined feed. Phosphoric acid recovered from the reactor residue contained about 93 pct of the P_2O_5 in the feed.

An averaged filtration rate of 745 lb $P_2O_5/ft^2/day$ was attained on digestion of the calcined shale product. Comparison of the two photomicrographs shows no significant differences in crystal size or form. Similarly, the digestion results as recorded in tables 2 and 3 show little difference except for a much more rapid filtration rate attained in digesting the calcined product. This averaged rate of 745 $lb/ft^2/day$ is lower than the rate of 900 lb $P_2O_5/ft^2/day$, which is a nominal phosphoric acid filter capacity obtained from a manufacturer's literature. The residue filter cakes from the calcined shale work had a firm sandy texture with no evidence of a muddy or thixotropic character. Two factors were major contributors to the lower filtration rates obtained from the shale feeds: First, the lower grade feeds gave more residue to filter for a given quantity of P_2O_5 produced; second, significantly higher quantities of carbonaceous and/or inert material in the shale would reduce filter rates.

Phosphoric Acid Quality

Impurities in the phosphoric acid prepared from calcined shale are compared in table 4 with filter acid prepared from high-grade western phosphate rock. Acid derived from calcined shale is higher in iron, aluminum, and

magnesium impurities than commercial acid. These higher impurity levels may be expected to increase sludge formation as acid is stored, and if acid is evaporated to merchant grade (54 pct P_2O_5), its viscosity may be higher. The effect of higher impurity levels in the manufacture of fertilizer and its subsequent agricultural use were not included in this investigation.

TABLE 4. - Comparison of impurities in filter acid derived from calcined shale and commercially produced filter acid, g/l

Acid sample	P_2O_5	Fe_2O_3	Al_2O_3	F	MgO
Calcined shale.....	355	12.8	24.1	19.1	15.5
Commercial.....	392	6.6	16.2	16.2	6.6

Studies are underway to evaluate solvent extraction methods as a means of selectively removing impurities from low-grade phosphoric acid.

CONCLUSIONS

Sulfuric acid digestion studies were performed on an intermediate-grade western phosphatic shale in a single-tank reactor system. Both uncalcined and calcined shale materials were digested to yield phosphoric acid with P_2O_5 recovery ranging from 92 to 96 pct.

Although high recovery of phosphate values could be achieved with the uncalcined shale, the filtration of the gypsum residue was very slow. The best filtration results, rates approaching commercial design values, were obtained when the shale was calcined to remove excess free carbon before digestion.

The impurity levels of iron, aluminum, and magnesium in the phosphoric acid derived from calcined shale were significantly higher than those in commercially prepared acid derived from high-grade western phosphate rock. Direct acidulation of intermediate-grade phosphatic shale shows promise as a method of recovering the phosphate from such source materials, if a method for removing or handling the impurities in the wet-process acid can be developed.

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